Crosslinkable Bicontinuous Cubic Assemblies via Mixtures of Gemini Amphiphiles and Butyl Rubber

Xiaoyun Lu[1], Brian J. Elliott*[2], and Douglas L. Gin*[1]

[1] Dept. of Chemistry & Biochemistry, and Dept. of Chemical & Biochemical Engineering, University of Colorado, Boulder, CO 80309
[2]TDA Research Inc., 12345 W. 52nd Ave., Wheat Ridge, CO 80033

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Introduction

Uses of Butyl Rubber (BR) as barrier material fabric

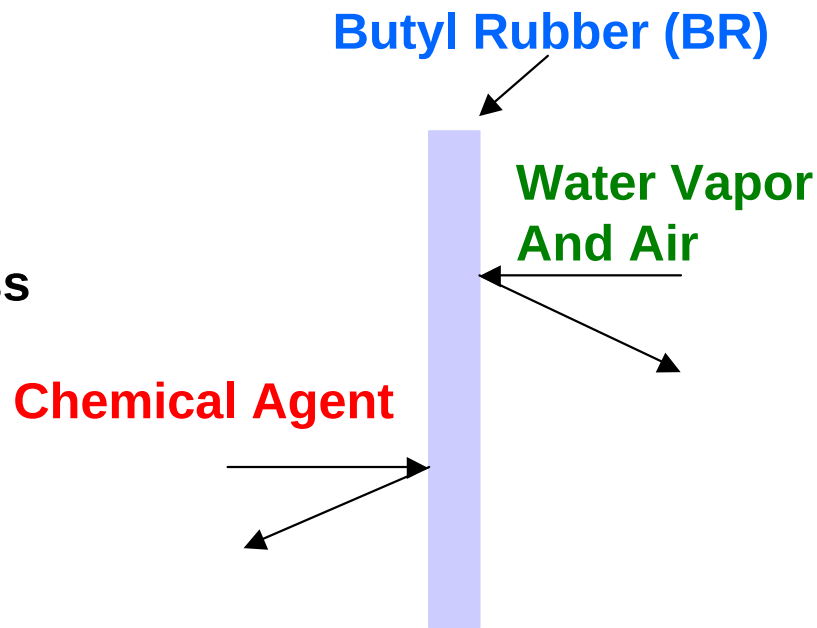
Advantages:

- **Low permeability toward organic solvents, and reactive chemicals**
- **Excellent chemical resistance**
- **Low cost**

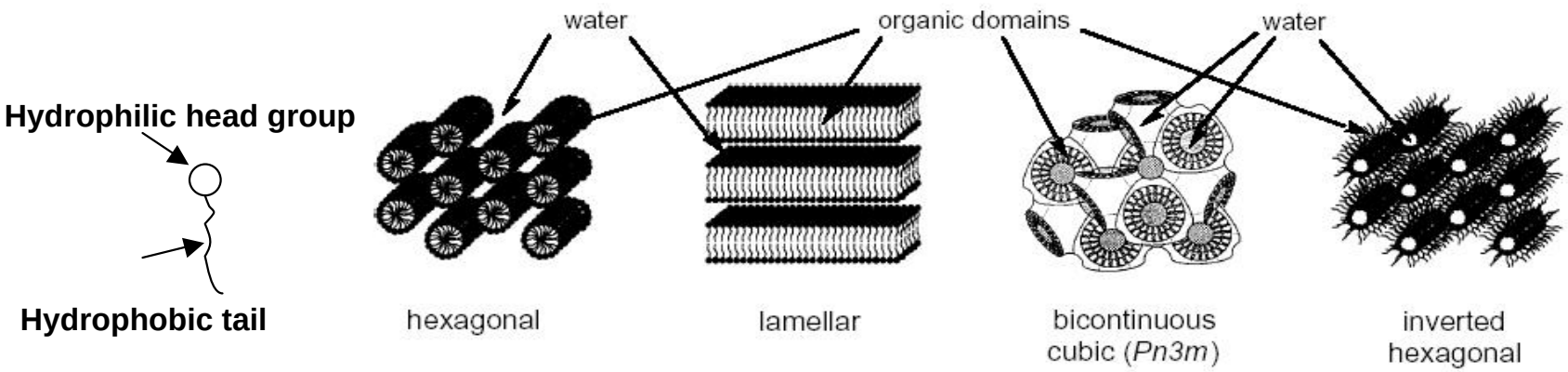
Disadvantages:

- **Lack of permeability of air and water vapor**

  ⇨ **Development of fatigue and heat stress in wearer**

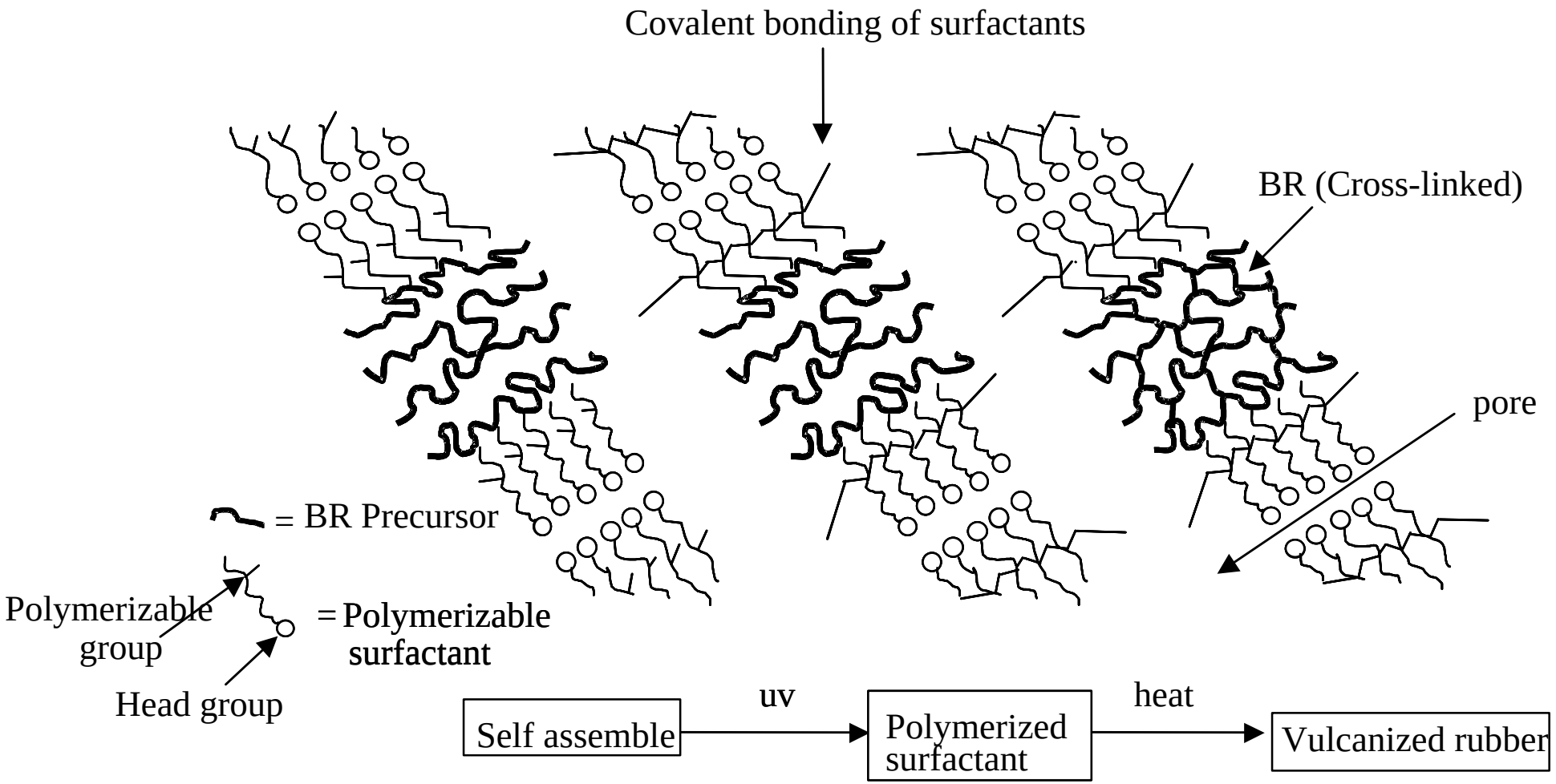


Overview of Lyotropic Liquid Crystals (LLCs)

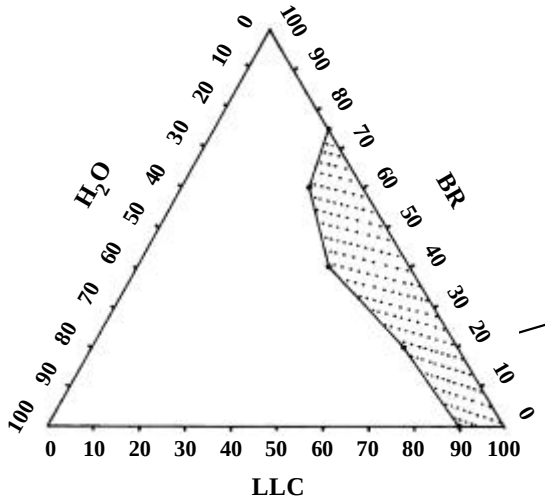


- **LLCs are amphiphilic molecules that can self-assemble into nanoporous structures.**
- **Multiple phases: hexagonal (H_I), lamellar (L), bicontinuous cubic (Q), inverted hexagonal (H_{II}), etc.**
- **Robust nanoscopic architectured material can be obtained upon crosslinking.**
- **Application: nanoscale reaction, separation, transportation, etc**

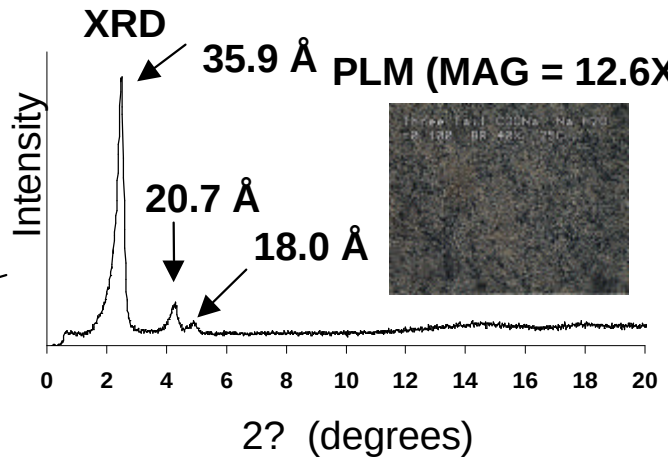
Approach: LLCs and BR Composites



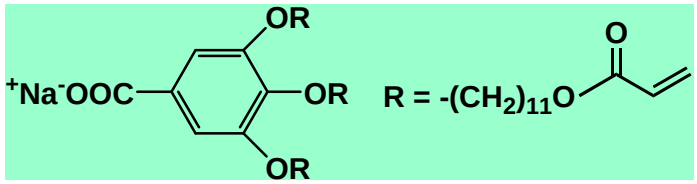
Prior Work in H_{II} Phase of LLC-1 / BR System



T = 23 °C



LLC-1: 60 %; BR: 40 %



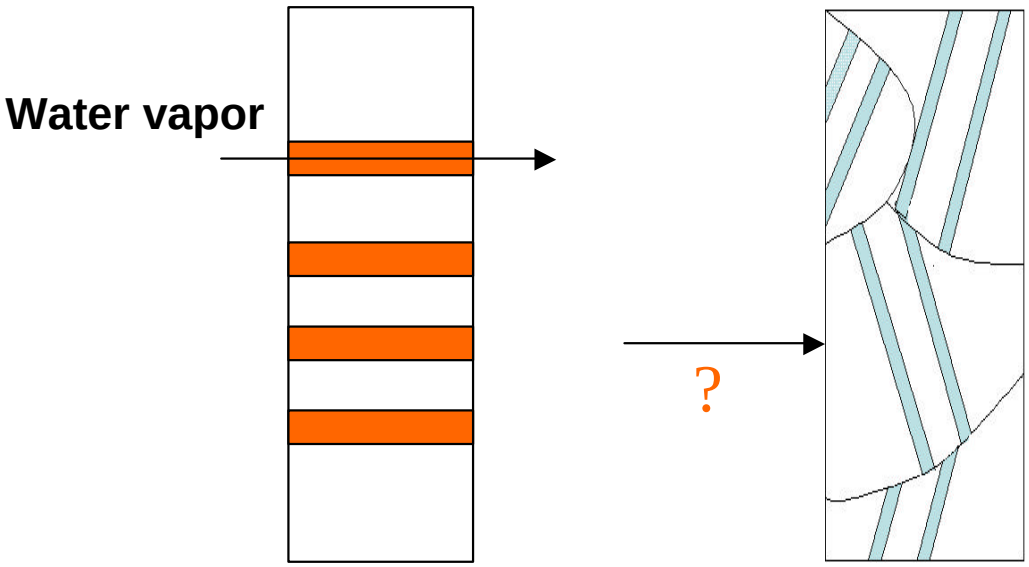
LLC - 1

- **LLC-1 retains H_{II} phase even with BR content as high as 75 wt %.**
- **Retention of H_{II} structure upon photo-initiated radical polymerization.**
- **Water vapor permeable and chemical agent simulant CEES impermeable.**

Done by Dr. Jizhu Jin

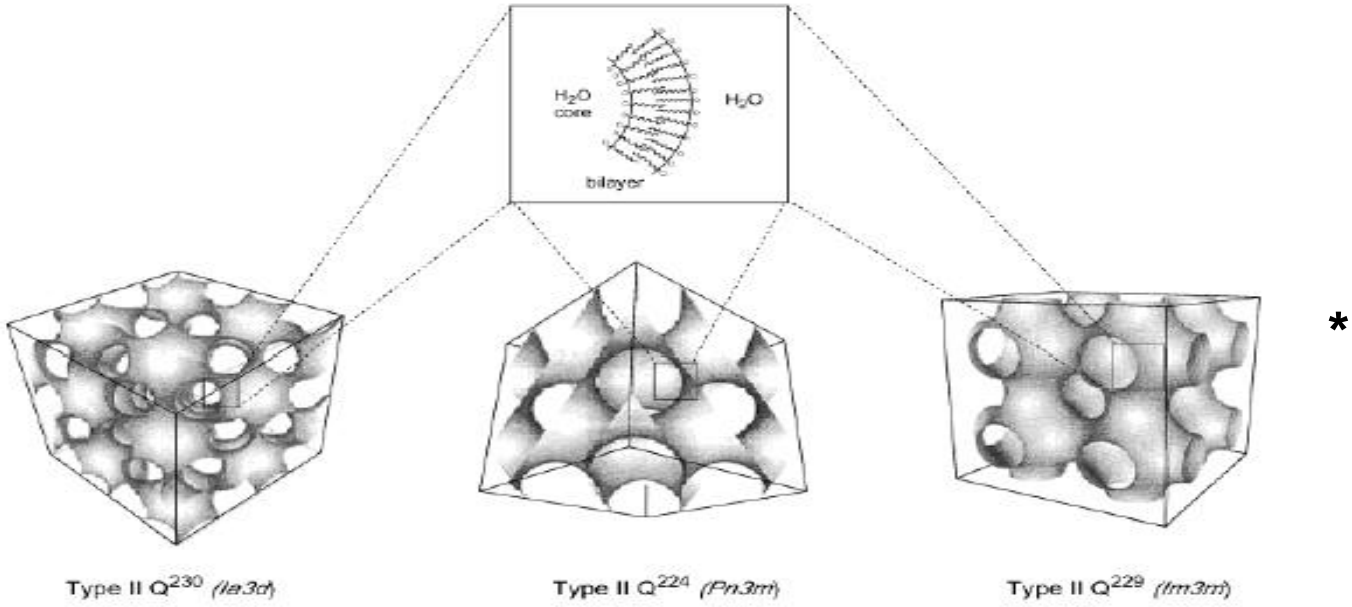
Problems in LLC-1/BR Composites

- **Requires pore alignment and continuity through material for maximum transportation.**
- **The acrylate ester tail is not hydrolytically stable.**



Perfect condition **Channels are blocked**

New objective: Bicontinuous Cubic Phases



*

- **Image of polarized light microscopy (PLM): Black (Pseudo isotropic)**
- **X-Ray diffraction(XRD): D-spacing proceeds in the ratio:**

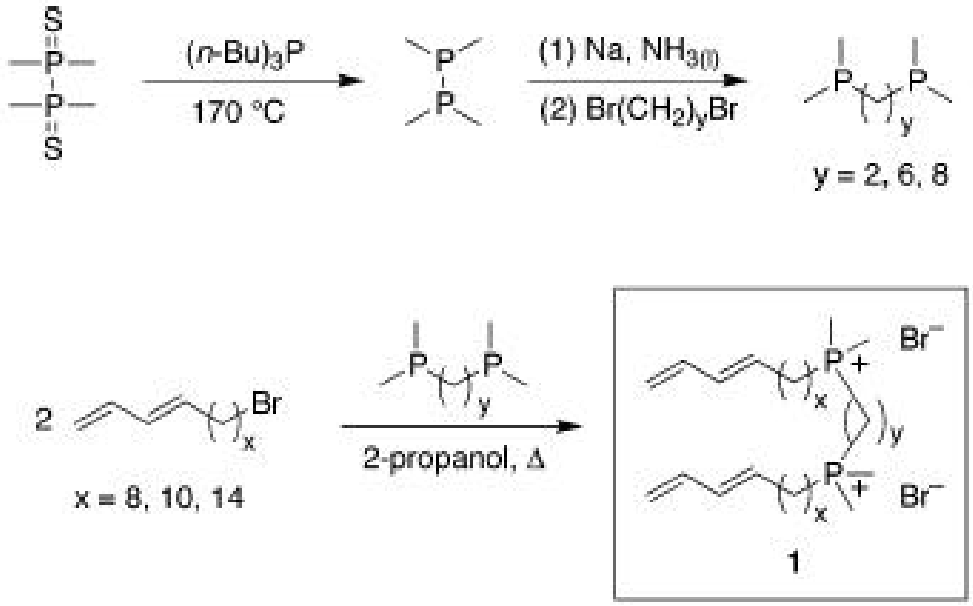
$$1 : 1/2^{1/2} : 1/3^{1/2} : 1/4^{1/2} : 1/5^{1/2} : 1/6^{1/2} : 1/7^{1/2} : 1/8^{1/2} \ldots$$

Advantage:

3-dimensional network of pores: eliminate the alignment problem

*Benedicto, A.D.; O'Brien, D.F. *Macromolecules*, **1997**, *30*, 3395-3402

Prior Work on Bicontinuous Cubic Phase LLC Monomers

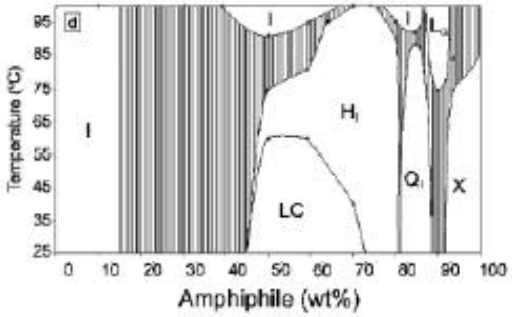


1a: x = 8; y = 2
1b: x = 8; y = 6
1c: x = 8; y = 8

1d: x = 10; y = 2
1e: x = 10; y = 6
1f: x = 10; y = 8

1g: x = 14; y = 2
1h: x = 14; y = 6
1i: x = 14; y = 8

Phase diagram of monomer 1e*



Disadvantage:

- **Brittle after cross-linking in pure form**

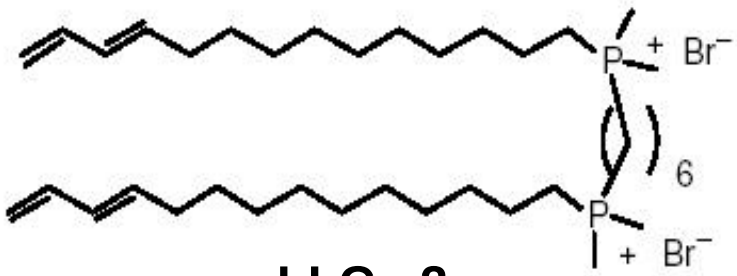
⇒ **Difficult to make barrier material**

***Pinzola, B.A.; Jin, J.Z.; Gin, D.L. *J.Am.Chem.Soc.* 2003, *125*, 2940-2949**

Research Objectives

- **Characterize composition and temperature ranges of LLC BR mixtures and specifically identify the bicontinuous cubic phase region**
- **Produce films of “breathable” cubic phase LLC- BR composites**
- **Characterize and optimize the polymerization of the surfactants and the vulcanization of the BR.**
- **Test the films for permeation of water vapor and rejection of chemical agent stimulants.**

Blending and copolymerizing of Gemini Monomers with BR

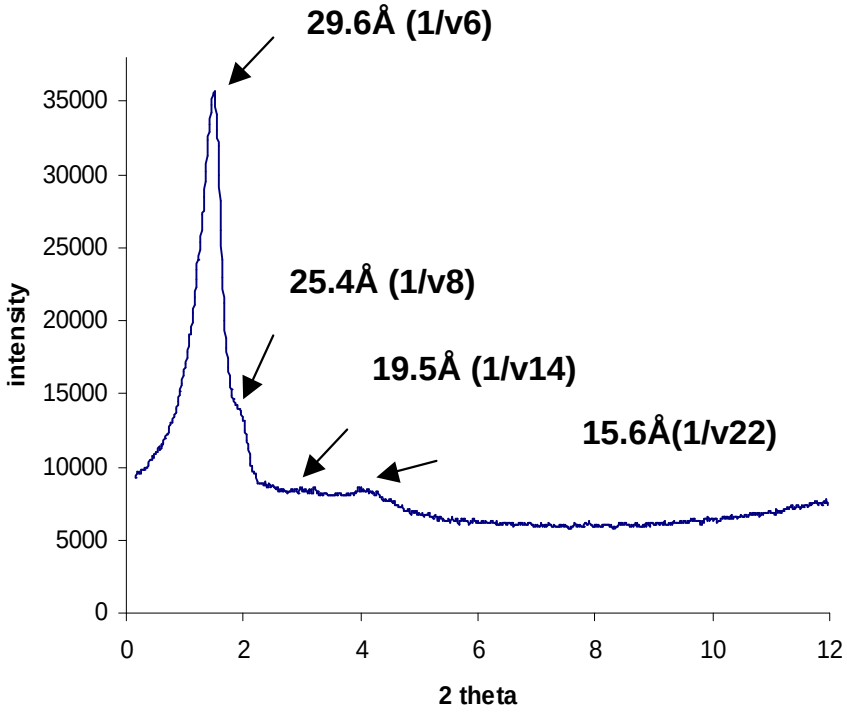


LLC - 2

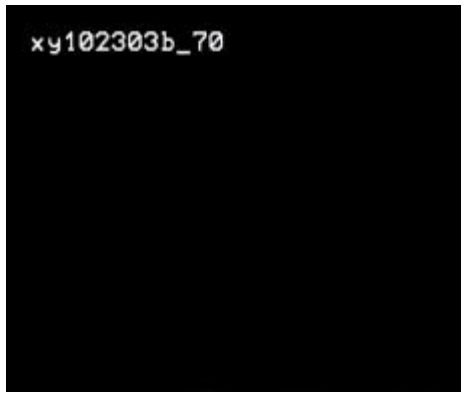
Blending Procedure

- **LLCs and H_2O were mixed in a glass vial and centrifuged three times (3800 RPM, 15 min.).**
- **Add the LLC mixture obtained in the above step with BR precursor solution (10 wt. % in hexane) and then mix/centrifuge three times (3800 RPM, 15 min.).**
- **Equilibrate above mixture for at least 16 hours at room temperature for testing.**

Characterization of Cubic Phase



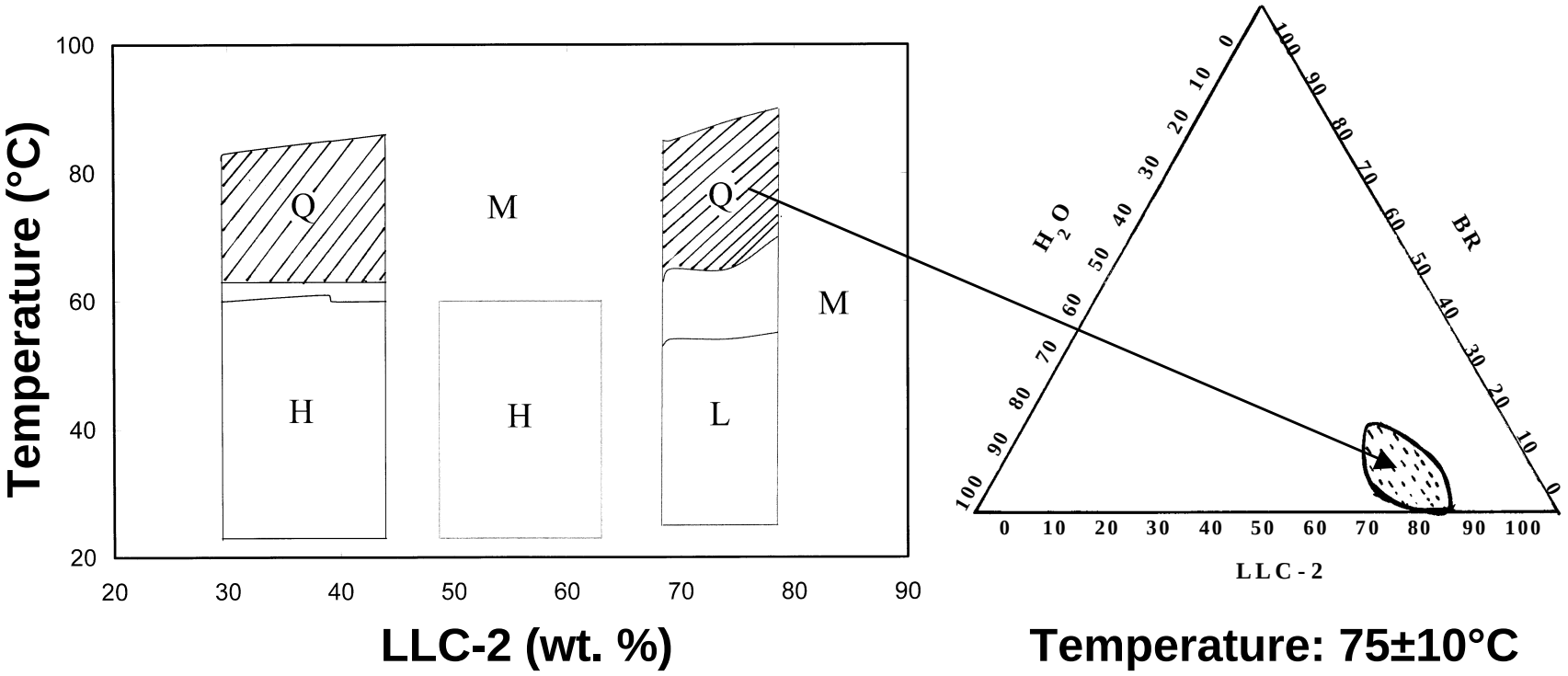
PLM (MAG = 12.6X)



69.1% LLC-2 26.9% H_2O 4.0% BR

- **Proof-of-concept for blending LLC with BR precursor with retention of cubic structure.**

Preliminary Phase Diagram of LLC - BR Composites



Q: Cubic; H: Hexagonal; L: Lamellar; M: Mixture;
Other regions are unidentified.

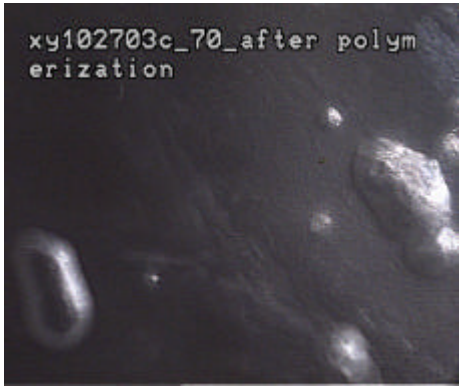
- **Cubic phase can be made at high temperature.**

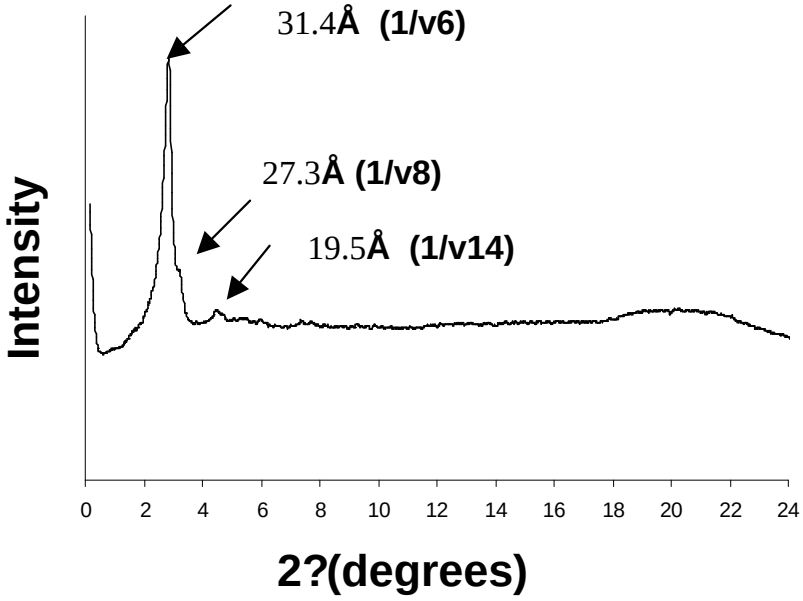
Polymerization of the Cubic phase LLC-BR composites

PLM (MAG = 12.6X)

Before polymerization

After polymerization





75.3% LLC-2 16.5% H_2O 8.2% BR

- **Retention of cubic phase upon radical polymerization**
- **The polymerized material is flexible.**
- **Degree of polymerization is to be done by IR.**

Processing to Make Membranes

- **Solvent casting – no retention of cubic phase after solvent evaporation**

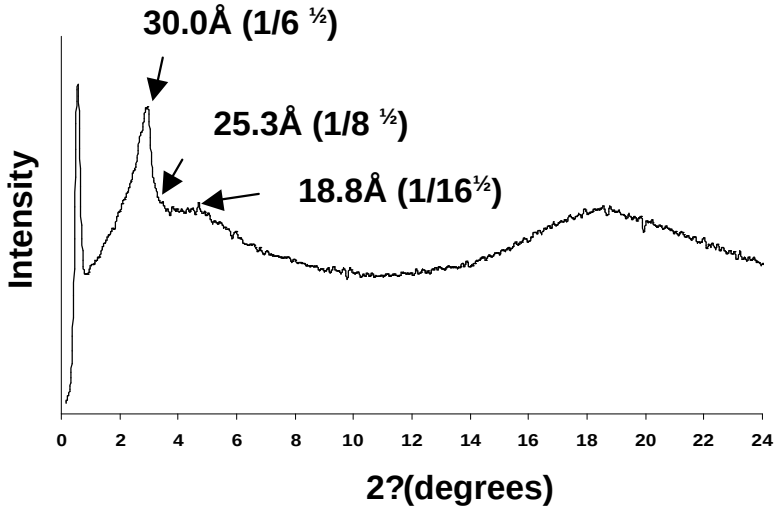
- **New method: Pressing**

  - **The LLC-BR precursor gel is put between two Mylar sheets and pressed by hydraulic press at room temperature**

  - **Heat up to 75±10°C to form the desired cubic phase**

  - **Cross-link to lock the structure**

XRD of above thin film



69.5% LLC-2 27.0% H_2O 3.5% BR

- **LLC-BR cubic phase can be formed as supported film for barrier application.**

Summary and Future Work

Summary

- **Bicontinuous cubic phase was made by blending and copolymerizing LLC surfactants and commercial BR.**
- **The material can be precessed and applied as thin films for barrier materials.**

Future Work

- **Explore better methods to make supported thin film**
- **Test mechanical properties of breathable cubic LLC-BR composites**
- **Test the permeation of Water vapor and chemical agent simulants with TDA Research**

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- **Dr. Jizhu Jin - Gin group**
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